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Tetrabutylammonium bis[*N*,*N*′-bis(4-chlorophenyl)pyridine-2,6-dicarboxamide(1−)]cobaltate(III) monohydrate

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The title complex, $(C_{16}H_{36}N)[Co(C_{19}H_{11}Cl_2N_3O_2)_2]\cdot H_2O$, contains two tridentate ligands having the pyridine-2,6-dicarboxamide stem. The appreciably compressed octahedral coordination around the Co atom is formed *via* the pyridine (py) N atom and two deprotonated amide N atoms of each ligand, with four five-membered chelate rings and two tridentate ligands in a meridional arrangement. For each ligand, the pyridine ring and the carbonyl groups are nearly coplanar, with torsion angles in the range 0.8 (10)–3.05 (10)°. Two intermolecular hydrogen bonds are formed between an uncoordinated water molecule and two carbonyl O atoms from different complex anions.

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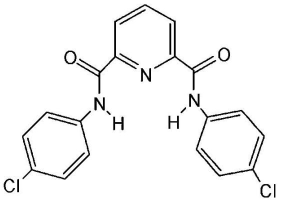
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.002 Å
Disorder in main residue
R factor = 0.048
wR factor = 0.121
Data-to-parameter ratio = 16.0

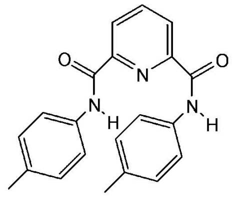
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

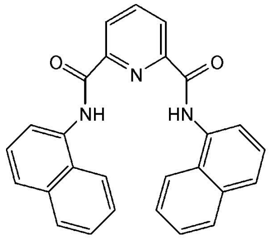
We have reported three new ligands (II), (III) and (IV) containing the 2,6-pyridinedicarboxamide stem in recent years (Qi *et al.*, 2001; Yang *et al.*, 2001; Qi, Yang *et al.*, 2003). All of them easily form Co^{3+} complexes by coordination of the pyridine and amide N atoms.



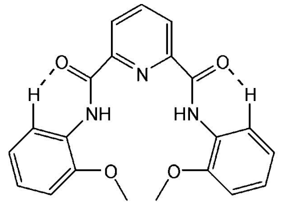
(I)



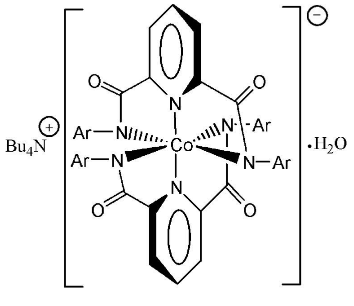
(II)



(III)



(IV)



Ar = 4-ClPh

(V)

However, Co^{3+} complexes of (III) and (IV) have been found to be difficult to crystallize because of the steric hindrance of the bulky naphthyl ring of ligand (III) or the 2-methoxy group on the benzene ring of ligand (IV). Only ligand (II), with the lesser steric effect of 4-methyl on the benzene ring on the coordinated amide N atom, has been used successfully to grow single crystals of a Co^{3+} complex for X-ray analysis (results not published). In order to explore further the electronic effect of the substituent group on the coordination chemistry of pyridinecarboxamide ligands toward metal ions,

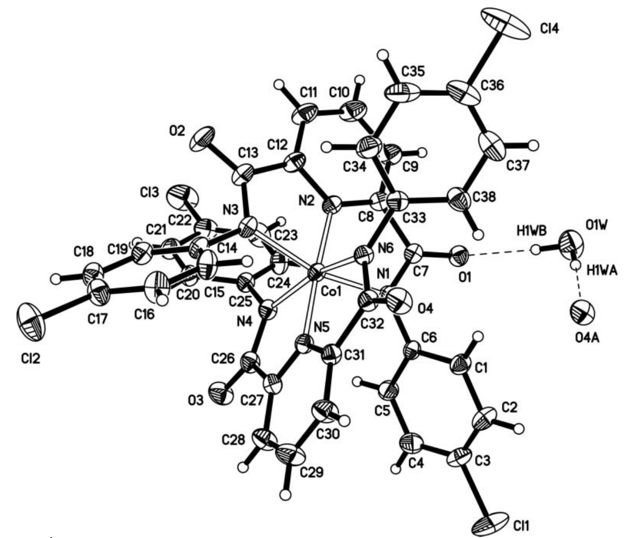


Figure 1
The structure of the anion and water molecule of (V), showing displacement ellipsoids drawn at the 30% probability level (dashed lines indicate hydrogen bonds) [Symmetry code: (A) $1 - x, 1 - y, -z$]

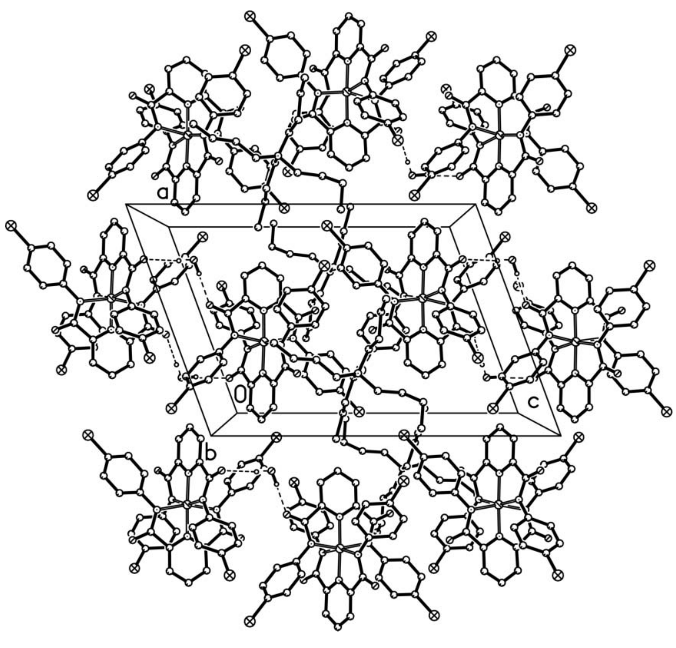


Figure 2
The packing, showing the alignment of anions in one layer. Dashed lines indicate hydrogen bonds. H atoms not involved in the hydrogen bonding have been omitted for clarity.

we synthesized the new ligand *N*,*N*′-bis(4-chlorophenyl)pyridine-2,6-dicarboxamide, (I).

As we expected, the electron-withdrawing effect of the chloro substituent on the benzene ring favors the coordination of the deprotonated nitrogen. The ligand (I), in its deprotonated form, coordinates to the metal Co^{3+} ion in the anion of the crystal structure of the title complex, (V). Each ligand (I) in complex (V) is also a roughly planar structure containing two five-membered chelate rings.

The structure of the anion of (V) in Fig. 1 shows that the four deprotonated amide N atoms are located in the equatorial plane and two pyridyl N atoms in the axial positions. The dihedral angle between the coordination planes N1–N3/Co1 and N4–N6/Co1 is 97.9 (2)°, indicating meridional coordination of the ligands. A very interesting feature of the structure is that the pendant chlorobenzene arms are oriented in space in a propeller-like fashion (Fig. 1). The dihedral angles between the benzene and pyridyl rings in one ligand, *viz*. C1/C2/C3/C4/C5/C6 and N5/C27/C28/C29/C30/C31, C14/C15/C16/C17/C18/C19 and N5/C27/C28/C29/C30/C31, are 40.6 (5) and 51.2 (5)°, respectively; while the dihedral angles between C20/C21/C22/C23/C24/C25 and N2/C8/C9/C10/C11/C12, C33/C34/C35/C36/C37/C38 and N2/C8/C9/C10/C11/C12 in the other ligand are 138.5 (4) and 139.6 (4)°, respectively, indicating that the two pairs of chlorobenzene arms have different propeller orientations.

The average $Co^{3+}-N_{amido}$ bond distance [1.9644 (9) Å] is slightly longer than the average $Co^{3+}-N_{pyridine}$ distance [1.8497 (9) Å]. As reported previously (Qi, Ma *et al.*, 2003; Qi *et al.*, 2004; Yang *et al.*, 2005), a feature of the structure is that central Co ion was oxidized from Co^{2+} to Co^{3+} by dioxygen in the air during the formation of the complex. The trivalent Co^{3+} and monovalent Bu_4N^+ balance the four deprotonated amide N atoms, forming a neutral complex.

The packing (Fig. 2) shows clearly that the anion and cation stack in alternate layers along the *c*-axis direction. Two intermolecular hydrogen bonds are formed by an uncoordinated water molecule and two carbonyl O atoms from different anions (Table 2).

Experimental

Ligand (I) was synthesized from 2,6-pyridinedicarboxylic acid and 3-chloroaniline following a published procedure (Ray *et al.*, 1997). The synthesis of complex (V) is described below. To a solution of cobalt dichloride (204 mg, 0.76 mmol) in DMF (10 ml) under a dinitrogen atmosphere was added $(Et_4N)[MeCO_2]\cdot 4H_2O$ (397 mg, 1.52 mmol), giving a blue–violet solution. Ligand (I) (738 mg, 1.52 mmol) was dissolved separately in DMF (15 ml) under a dinitrogen atmosphere; NaH (72.92 mg, 3.04 mmol) was added to the mixture which was stirred for 45 min, producing a light-yellow solution. The two solutions were then mixed, and a color change from the initial orange to yellowish brown with a green tinge was observed. On exposure to air, the color of the solution darkened. After being stirred for 4 h, the reaction mixture was filtered and the solvent was removed *in vacuo*. To the solid thus obtained was added MeCN (18 ml), and the solution was filtered. Slow evaporation of this solution in air resulted in the formation of dark-green crystals. The crystal used for the data collection was obtained by slow evaporation of a saturated solution in DMF–water (2:3) at room temperature.

Crystal data

$(C_{16}H_{36}N)[Co(C_{19}H_{11}Cl_2N_3O_2)_2]\cdot H_2O$
$M_r = 1087.82$
Monoclinic, $P2_1/n$
$a = 12.9275$ (17) Å
$b = 24.350$ (3) Å
$c = 18.267$ (2) Å
$\beta = 110.154$ (3)°
$V = 5398.2$ (12) Å^3
$Z = 4$
$D_x = 1.338$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.57$ mm^{-1}
$T = 293$ (2) K
Prism, red
0.36 × 0.26 × 0.22 mm

m160 Qi *et al.* • $(C_{16}H_{36}N)[Co(C_{19}H_{11}Cl_2N_3O_2)_2]\cdot H_2O$ *Acta Cryst.* (2007). E**63**, m159–m161

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.742$, $T_{max} = 1.000$ (expected range = 0.655–0.882)
36197 measured reflections
12510 independent reflections
6725 reflections with $I > 2\sigma(I)$
$R_{int} = 0.057$
$\theta_{max} = 27.7°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.121$
$S = 1.00$
12510 reflections
780 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.048P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.009$
$\Delta\rho_{max} = 0.36$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co1—N1	1.9638 (7)	Co1—N4	1.9688 (8)
Co1—N2	1.8466 (7)	Co1—N5	1.8535 (7)
Co1—N3	1.9673 (8)	Co1—N6	1.9592 (8)
N2—Co1—N5	177.35 (3)	N1—Co1—N4	93.15 (3)
N2—Co1—N1	80.95 (3)	N2—Co1—N4	100.36 (3)
N5—Co1—N1	96.91 (3)	N3—Co1—N4	89.18 (3)
N6—Co1—N1	89.82 (3)	N5—Co1—N4	81.28 (3)
N2—Co1—N3	81.54 (3)	N6—Co1—N4	162.71 (3)
N5—Co1—N3	100.61 (3)	N2—Co1—N6	96.94 (3)
N6—Co1—N3	93.10 (3)	N5—Co1—N6	81.45 (3)
N1—Co1—N3	162.47 (3)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*WA*···O4^{i}	0.86	1.99	2.8487 (11)	177.4
O1*W*—H1*WB*···O1	0.86	2.00	2.8588 (12)	173.8

Symmetry code: (i) $-x+1, -y+1, -z$.

C-bound H atoms were positioned geometrically, with C—H = 0.93–0.97 Å, and refined using the riding-model approximation [$U_{iso}(H) = 1.2U_{eq}(C)$]. Water H atoms were located in difference Fourier maps. The O—H distances were constrained to 0.86 Å, then refined using the riding-model approximation. [$U_{iso}(H) = 1.2U_{eq}(O)$].

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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Acta Cryst. (2007). E**63**, m159–m161 Qi *et al.* • $(C_{16}H_{36}N)[Co(C_{19}H_{11}Cl_2N_3O_2)_2]\cdot H_2O$ **m161**